



Impact of solid fuel combustion technology on valence speciation of chromium in fly ash



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HIGHLIGHTS

- Biomass and high combustion temperature favor enrichment of fly ash with Cr(VI).
- Biomass combustion favor enrichment of fly ash with water soluble Cr(VI).
- Alkali compounds and Fe oxides play a key role in shaping Cr(VI/III) speciation.
- Cr(VI) level in coal fly ash drops in order: PCC boiler \gg FBC boiler \approx SF boiler.
- An influence of combustion technologies on Cr speciation in fly ash was explained.

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ABSTRACT

Fly ash (FA) generated in real furnaces was used to evaluate the impact of the kind of the solid fuel burnt and combustion technology on chromium speciation, particularly the presence of Cr(III) and Cr(VI) forms as well as readily and hardly leachable chromium(VI) species in FAs. The FAs originated from a pulverized coal combustion boiler (PCC boiler), a fluidized bed combustion boiler (FBC boiler), a stoker-fired boiler (SF boiler), a municipal solid waste incinerator (MSWI), a cement rotary kiln (CRK) and a modern domestic boiler (DB). The speciation analysis of chromium was carried out by means of extraction followed by catalytic cathodic stripping voltammetry with adsorption of Cr(III)-DTPA complexes (CCSV-DTPA) for determination of Cr(VI) and AAS was used for determination of Cr content.

It has been revealed that the antagonistic action of alkali metal compounds and iron oxides plays a crucial role in shaping valence speciation of chromium. According to the proposed transformation path of oxidation of Cr(III) to Cr(VI), hard coal combustion in an SF boiler, an FBC boiler or a domestic boiler will generate FAs with a low Cr(VI) level. Replacing fuel with biomass should create favorable conditions for generating FA enriched with Cr(VI). Relatively high concentrations of Cr(VI) can also be expected in FA generated in the process of high-temperature combustion of coal in PCC boilers.

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1. Introduction

Chromium speciation in fly ash has been studied for a number of years and were focused on the mode of chromium occurrence as well as the mechanism of chromium transformation in a combustion chamber. The determination of chromium(III) and chromium(VI) has been carried out directly in a FA sample by using non-destructive techniques [1–5] or indirectly by extraction followed by determination of released chromium species [2,6–8]. The interest in chromium valence speciation in FA stems from a significant difference in toxicity and bioavailability of the

Cr(III)- and Cr(VI)-species. Cr(III) is a bioelement, whereas particulate Cr(VI) is regarded as a factor which increases the severity of ongoing allergic asthma and alters its phenotype [9]. The environmental impact and health effects are related to chromium(VI) load in the environment.

The scale of the problem is large, although it cannot be determined accurately, as Cr(VI) emission is inventoried only in relatively few countries. Within the last twenty years the EU (15) countries produced annually 40 Tg of FA on average, of which 92% was utilized in 2006. The construction industry and underground mining used 20 Tg (concrete addition – 26.7%, cement raw material – 25.8%, road construction and filling applications – 22.5%, blended cement – 11.3%, concrete blocks – 7.1%, infills – 4%, and others – 2.6%) [10]. The remaining FA was used in land reclamation and

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restoration. In that same year in the USA 72 Tg of FA was generated, of which 32 Tg was utilized (the construction industry – 60% and mining and earthworks – 40%) [11]. If we assume that 3 mg/kg is the expected value of Cr(VI) content in FA [2,4,7,8,12] and that utilization of only a half of the FA generated creates conditions for Cr(VI) release, the environment in Europe is loaded annually with 60 Mg of Cr(VI). Although this value is high, it seems to be correct. For comparison, total annual emissions of Cr(VI) in the US were 44 Mg in 2002 [13]. Proportionally lower Cr(VI) emissions to air were found in the UK – 28.6 Mg/year (2008) [14], Australia – 2.5 Mg/year (2011) [15] and Canada – 1 Mg/year (2010) [16].

In order to reduce the Cr(VI) pollution burden on the environment, it is crucial to control oxidation of Cr(III) to Cr(VI) taking place during combustion of solid fuels in such a way that it is possible to reduce the Cr(VI) content or, at least, to limit Cr(VI) elution from FA.

Although Cr valence speciation in various coals and coal combustion products has been covered quite extensively in the literature, and moreover recently a number of papers have been published in which the authors proposed a mechanism of possible chromium transformations [3,5,6,17,18], there is still a lack of a general approach which would explain the essence of shaping Cr speciation in FA generated in real furnaces based on various combustion technologies.

The aim of our work is to examine the speciation of Cr(III/VI) and speciation of Cr(VI) (water leachable and hardly leachable fractions) in FAs depending on which combustion technology of solid fuel has been used. FAs produced in pulverized fuel boilers, stoker-fired boilers, a fluidized bed boiler, an up-draught combustion

domestic boiler, a Krüger grate furnace and a cement rotary kiln have been investigated. An attempt has been made to prepare an outline of a chromium transformation model in real solid fuel fired boilers which may explain the differences in chromium valence speciation observed in the generated FAs.

2. Experimental

2.1. Sampling and samples preparation

FA samples (1 kg) were collected from various parts of dust arresting systems. Pulverized fuel combustion FA samples were collected from each of the three fields of an electrostatic precipitator system. Both units, in which hard coal was fired and biomass was co-fired ($C/B = 9:1$), were of the same type and worked in the same coal-fired power plant. The samples were denoted as PCC/FA-I/1-3 and PCC/FA-II/1-3 for coal and coal/biomass combustion, respectively (Table 1). The stoker-fired coal fly ash samples were collected from collection tanks of the multicyclone and a battery of cyclones in two heating plants (I and II) equipped with the same type of stoker-fired boilers. The samples were denoted as SF/FA, 1 – multicyclone and 2 – battery of cyclones and the subscripts *a* and *b* stand for fraction $>63 \mu\text{m}$ (coarse fraction) and $\leq 63 \mu\text{m}$ (fine fraction), respectively. Three FA samples denoted as FBC/FA-1, FBC/FA-2 and FBC/FA-3 were collected from the ash hopper of the ESP in the FBC boiler system which was supplied with hard coal from three coal mines, one from Lublin Basin (1) and two from Upper Silesian Basin (2 and 3). In this installation dry limestone was injected into the flue gases before the collection of particulate

Table 1
Kind of furnace, fuel, dust collection device and sampling points.

| No | Fly ash sample | Furnace | Fuel | Temperature of burning zone | Dust collection device | Sampling point ^a /remarks | |
|----|----------------|---------------------------------------|--|-----------------------------|--|--|----------------------------------|
| 1 | PCC/FA-I/1 | Pulverized-fuel boiler | Hard coal energy value – 22 MJ/kg, ash – 20%, sulfur – 1.1%. Particle size <0.1 mm. Hard coal (ditto) + wood waste (10%) energy value of biomass – max. 18 MJ/kg | 1800–1935 °C | ESP | 1st-field ESP | |
| 2 | PCC/FA-I/2 | | | | | 2nd-field ESP | |
| 3 | PCC/FA-I/3 | | | | | 3rd-field ESP | |
| 4 | PCC/FA-II/1 | | | | | 1st-field ESP | |
| 5 | PCC/FA-II/2 | | | | | 2nd-field ESP | |
| 6 | PCC/FA-II/3 | | | | | 3rd-field ESP | |
| 7 | SF/FA-I/1a | Stoker-fired boiler | Hard coal energy value – 23.2 MJ/kg, ash – 15.1%, sulfur – 0.63%, moisture content – 11.8% | 1100 °C | 1. Multicyclone | $\varphi > 63 \mu\text{m}$ (42%) | |
| 8 | SF/FA-I/1b | | | | | $\varphi \leq 63 \mu\text{m}$ (58%) | |
| 9 | SF/FA-I/2a | | | | | 2. Cyclone | $\varphi > 63 \mu\text{m}$ (52%) |
| 10 | SF/FA-I/2b | | | | | $\varphi \leq 63 \mu\text{m}$ (48%) | |
| 11 | SF/FA-II/1a | Stoker-fired boiler | Hard coal energy value – 21.9 MJ/kg, ash – 19.5%, sulfur – 0.62%, moisture content – 10.2% | 1100 °C | 1. Multicyclone | $\varphi > 63 \mu\text{m}$ (40%) | |
| 12 | SF/FA-II/1b | | | | | $\varphi \leq 63 \mu\text{m}$ (60%) | |
| 13 | SF/FA-II/2a | | | | | 2. Cyclone | $\varphi > 63 \mu\text{m}$ (57%) |
| 14 | SF/FA-II/2b | | | | | $\varphi \leq 63 \mu\text{m}$ (43%) | |
| 15 | FBC/FA-1 | Fluidized-bed boiler | Hard coal energy value – 21.1 MJ/kg, ash – 21.1%, sulfur – 1.04% | 850–865 °C | ESP preceded by dry limestone injection | Collection tank | |
| 16 | FBC/FA-2 | | | | | Hard coal energy value – 22.1 MJ/kg, ash – 21.4%, sulfur – 0.52% | |
| 17 | FBC/FA-3 | | | | | Hard coal energy value – 22.9 MJ/kg, ash – 20.7%, sulfur – 0.42% | |
| 18 | DB/FA-1 | Up-draught combustion domestic boiler | Pine wood briquette | | Lack | Dead space of flue | |
| 19 | DB/FA-2 | | | | | | Birch plywood briquette |
| 20 | MSWI/FA | Krüger grate furnace (incinerator) | Sorted municipal wastes | 1000–1100 °C | Bag filter preceded by hydrated lime injection | | |
| 21 | CRK/FA-1 | Cement rotary kiln | Hard coal energy value – 27 MJ/kg, ash – 7.0%, sulfur – 1.2%, moisture content – 8.5% + alternative fuel/wood waste | Max. 2000 °C | 1. Dust chamber 2. Two parallel bag filters | 1st bag filter | |
| 22 | CRK/FA-2 | | | | | | |
| 23 | CRK/FA-3 | | | | | 2nd bag filter | |

^a If different than the one given in the dust collection device column.

matter in ESP. A sample of FA generated by incineration of the combustible fraction of municipal solid wastes (denoted as MSWI/FA) was collected from a bag house filter. In this installation hydrated lime was injected into the flue gases before the dust collector. FA generated in a cement rotary kiln fired with a mixture of coal and an alternative fuel was captured in the dust chamber and then in two parallel bag filters. The FA samples are denoted as CRK/FA-1, CRK/FA-2 and CRK/FA-3, respectively. The up-draught combustion boiler (nominal output of 20 kW), commonly used in Poland for individual house heating, was fired with pinewood briquettes and birch-plywood briquettes. The FA samples were collected from the flue at the reversal gas spot where the so-called dead space enabled the accumulation of FA particulates (hereforth designated as DB/FA-1 and DB/FA-2, respectively).

Directly after collection all samples were stored in hermetically sealed plastic containers. The SF/FA samples were sieved through a sieve of 63 μm . In both the SF boilers ca. 40 wt% of FA retained in the multicyclone had a dimension $\leq 63 \mu\text{m}$, and somewhat below 50 wt% of FA trapped in the cyclone had a dimension $\leq 63 \mu\text{m}$.

2.2. Determination of the contents of chromium and other metals

The environmentally available metal content in the FA samples (pseudo total metal concentration) was determined via microwave-assisted digestion of the samples with $\text{HNO}_3/\text{H}_2\text{O}_2$ according to the manufacturer's protocol (Milestone, 1992) [19]. Three sub-samples were digested simultaneously for each FA sample.

The concentration of metals in the digest samples was determined using an atomic absorption spectrometer AAS – Agilent Technologies 200 Series AA 240 FS AA. The limits of determination for chromium and other metals being examined were: Cr – 2.7 mg/kg, Ca – 0.9 mg/kg, Fe – 3.8 mg/kg, K – 2.1 mg/kg and Na – 1.4 mg/kg.

2.3. Determination of chromium(VI) content

Leaching of total Cr(VI) from the FA samples was carried out similarly as described in the EPA 3060A method (US EPA, 1996) [20]. A 0.5 g sample was being extracted in 10 mL $\text{Na}_2\text{CO}_3/\text{NaOH}$ for 1 h at 95 °C.

Soluble Cr(VI) was released by shaking a 1 g FA sample in 10 mL of deionised water for 24 h at RT according to the leaching test described in PN-EN 12457-2:2006 [21].

The leachates were filtered through a 0.45 μm nitrate-cellulose membrane filter.

Determination of Cr(VI) in leachates was performed using the technique of CCSV-DTPA. Voltammograms were recorded with a Trace Analyzer Model 394 connected to a hanging mercury drop working electrode Model 303A SMDE (EG&G Princeton Applied Research). LOD (instrumental) was found to be 2.9 $\mu\text{g/L}$ (0.0026 mg/kg of FA).

CMR061-030 (sandy loam) was used as a certified reference material to validate the analytical procedure. Cr(VI) extraction was carried out in the same way as for FA samples. It was found that the content of Cr(VI) was 239.3 mg/kg ($n = 3$), the certified value was $241.00 \pm 9.00 \text{ mg/kg}$, hence the recovery was 99.3%.

2.4. ORP and pH determination

The pH of the water extracts was measured using a Mettler Toledo SevenEasy pH-meter (Mettler Toledo, 2006), and the Oxidation–Reduction Potential (ORP) with a single rod electrode (HI-3230, 3.3 mol/L silver chloride electrode, Hanna Instruments, Portugal).

3. Results and discussion

3.1. Occurrence of chromium and other metals

Chromium content in tested samples varies within relatively narrow range limits (Table 2). The lowest concentrations of chromium were found in FA from combustion of wood fuels (DB/FA-1 and DB/FA-2). In the majority of coal-FA samples chromium occurs at the level of 50–100 mg/kg, 81 mg/kg on average. High chromium contents were found in the FA captured at the second stage of dust arresting of flue gases in a cement rotary kiln, 228.3 mg/kg and 242.3 mg/kg. In this case, the presence of chromium only partially has its source in the coal being burnt. The components of burnt clinker and the alternative fuel (a fraction of municipal wastes) have a considerable share in the chromium content. This can be indirectly confirmed by high contents of alkali metals in CRK/FA samples, e.g. potassium content was 15 times higher than its average content in FA generated in power and heating plants. The contents of chromium determined in this work are well within typical values for FA from other power plants: 49–144 mg/kg [8], 18–130 mg/kg [7], 26–50 mg/kg [22], and 71 mg/kg [23]. The chromium content in FA from MSWI (97.3 mg/kg) corresponds to the level of chromium in coal-FA samples and is lower than chromium content given in previous studies on MSWI-FA: 306–341 mg/kg (fraction passed through a # 50 sieve) [24], 127–175 mg/kg [12], 340–770 mg/kg [25], and 407 mg/kg [26]. In this case it is hard to expect a close similarity of results due to the fact that the chemical composition of MSWI-FA, including chromium, was strongly conditioned by the kind of MSW fractions being burnt.

Other metals (K, Na, Ca and Fe) were examined due to the potential role of their compounds in shaping valence speciation of chromium [3,5,6,17,27]. Generally, coal-FA generated in SF boilers and FBC boilers is more enriched in metals regarded as major elements than PCC/FA. As expected, wood-FA was characterized by higher K and Ca contents than coal-FA (PCC/FA and SF/FA). Co-combustion of biomass (10%) in a PCC boiler resulted only in a slight increase in the concentration of K. It is worth noting that the increased concentration of Ca in FBC/FA samples (av. 44 g/kg) and the high concentration in the MSWI/FA sample (306 g/kg) result from desulfurization of flue gases by means of a controlled dosing of limestone and hydrated lime, respectively. The environmentally available Fe varies within a relatively wide range from 3.29 g/kg (MSWI/FA) to 42.0 g/kg (SF/FA). Its concentrations in coal-FA samples from the PCC boiler were lower than those from the SF and FBC boilers.

Some interesting conclusions can be drawn from the results of the distribution of the metals in grain fractions of FA. In order to quantitatively characterize this phenomenon, the values of enrichment factor (EF) for SF/FAs were calculated as a quotient of the concentration of the metal in fine fraction ($\leq 63 \mu\text{m}$) and in coarse fraction ($> 63 \mu\text{m}$) (Fig. 1), whereas EFs for PCC/FAs as a quotient of metal concentration in the 2nd-field or 3rd-field ESP fraction and in the 1st-field ESP fraction (Fig. 2).

In the process of mid-temperature coal combustion ($< 1100 \text{ }^\circ\text{C}$) the finer fractions become enriched in all the metals of interest, although not to the same degree: $\text{Cr} > \text{K} > \text{Na} > \text{Fe} \approx \text{Ca}$. The distribution of these elements in ESP fractions of PCC-FA were different. The finer FA fractions are enriched in Cr, K and Na and depleted in Ca and Fe. As the condensation of volatile elements on the surfaces of FA particles in the post-combustion zone results in surface enrichment [28], it can be assumed that the surfaces of PCC-FA particles are covered with Cr, Na and K compounds, whereas in SF boilers the compounds of Ca, Cr, K, Na and Fe condense as a coating on FA particles.

Table 2
Metal content in the fly ashes samples and the characteristics its water extracts.

| No | Sample | Fly ash | | | | Water extract | | | | | | | | | |
|----|-------------|--------------|--------------|--------------|-------------|---------------|----------------|--------------------------------|------------------------------------|------------------------------|-----|----------|----|--|--|
| | | K (g/kg) | Na (g/kg) | Ca (g/kg) | Fe (g/kg) | Cr (mg/kg) | Cr(VI) (mg/kg) | Cr(VI) _{sol.} (mg/kg) | Cr(VI) _{h.leach.} (mg/kg) | Cr(VI) (μg/dm ³) | pH | ORP (mV) | rH | | |
| 1 | PCC/FA-I/1 | 2.94 ± 0.13 | 2.08 ± 0.15 | 21.48 ± 0.58 | 18.2 ± 1.2 | 30.6 ± 2.8 | 3.20 ± 0.20 | 0.504 ± 0.034 | 50.4 ± 3.4 | 12.21 | -44 | 29.2 | | | |
| 2 | PCC/FA-I/2 | 3.09 ± 0.16 | 2.42 ± 0.12 | 16.7 ± 1.3 | 17.7 ± 1.0 | 51.9 ± 2.2 | 5.95 ± 0.18 | 1.837 ± 0.058 | 183.8 ± 5.8 | 12.16 | -57 | 28.7 | | | |
| 3 | PCC/FA-I/3 | 4.19 ± 0.14 | 3.14 ± 0.19 | 13.71 ± 0.39 | 16.8 ± 1.0 | 75.2 ± 3.4 | 7.20 ± 0.89 | 3.15 ± 0.11 | 315.3 ± 11 | 11.46 | -29 | 28.2 | | | |
| 4 | PCC/FA-II/1 | 2.84 ± 0.10 | 1.94 ± 0.13 | 16.52 ± 0.27 | 13.2 ± 0.4 | 51.8 ± 1.7 | 4.97 ± 0.54 | 2.49 ± 0.23 | 249 ± 23 | 12.22 | -9 | 30.4 | | | |
| 5 | PCC/FA-II/2 | 3.66 ± 0.11 | 2.26 ± 0.17 | 13.43 ± 0.16 | 12.0 ± 0.2 | 55.1 ± 1.0 | 5.01 ± 0.11 | 2.93 ± 0.15 | 293 ± 15 | 11.81 | -16 | 29.4 | | | |
| 6 | PCC/FA-II/3 | 5.37 ± 0.17 | 3.43 ± 0.13 | 9.96 ± 0.14 | 11.9 ± 0.2 | 60.8 ± 3.2 | 4.88 ± 0.37 | 3.09 ± 0.14 | 309 ± 14 | 9.56 | 80 | 28.1 | | | |
| 7 | SF/FA-I/1a | 6.45 ± 0.19 | 5.62 ± 0.19 | 15.6 ± 2.0 | 15.8 ± 1.2 | 67.7 ± 3.1 | 0.695 ± 0.090 | 0.0167 ± 0.0076 | 1.68 ± 0.10 | 9.59 | 115 | 29.4 | | | |
| 8 | SF/FA-I/1b | 17.89 ± 0.26 | 12.49 ± 0.29 | 22.91 ± 0.27 | 25.6 ± 1.0 | 201.0 ± 6.0 | 0.939 ± 0.050 | 0.0423 ± 0.0034 | 4.23 ± 0.34 | 8.05 | 197 | 29.1 | | | |
| 9 | SF/FA-I/2a | 9.33 ± 0.25 | 7.87 ± 0.24 | 18.31 ± 0.32 | 20.1 ± 1.1 | 70.9 ± 1.8 | 0.985 ± 0.092 | 0.0126 ± 0.0019 | 1.26 ± 0.19 | 7.73 | 161 | 27.2 | | | |
| 10 | SF/FA-I/2b | 18.96 ± 0.32 | 13.05 ± 0.20 | 20.4 ± 1.8 | 22.6 ± 1.2 | 228 ± 25 | 1.237 ± 0.028 | 0.0463 ± 0.0026 | 4.64 ± 0.25 | 7.12 | 179 | 26.6 | | | |
| 11 | SF/FA-II/1a | 8.9 ± 1.1 | 11.58 ± 0.76 | 27.0 ± 1.1 | 26.4 ± 3.7 | 48.7 ± 9.9 | 0.313 ± 0.011 | 0.0072 ± 0.0029 | 0.72 ± 0.22 | 9.78 | 94 | 29.0 | | | |
| 12 | SF/FA-II/1b | 16.10 ± 0.14 | 17.71 ± 0.95 | 35.4 ± 1.2 | 42.0 ± 1.1 | 100.5 ± 5.1 | 0.336 ± 0.031 | 0.0162 ± 0.0079 | 1.60 ± 0.11 | 8.71 | 138 | 28.4 | | | |
| 13 | SF/FA-II/2a | 7.34 ± 0.98 | 9.5 ± 1.1 | 13.9 ± 3.8 | 14.2 ± 1.2 | 38.8 ± 1.3 | 0.398 ± 0.018 | 0.0065 ± 0.0011 | 0.65 ± 0.11 | 9.67 | 102 | 29.1 | | | |
| 14 | SF/FA-II/2b | 17.80 ± 0.64 | 20.45 ± 0.55 | 27.5 ± 1.4 | 29.9 ± 4.1 | 85.1 ± 4.2 | 0.623 ± 0.049 | 0.0227 ± 0.0012 | 2.27 ± 0.11 | 8.92 | 132 | 28.6 | | | |
| 15 | FBC/FA-1 | 12.04 ± 0.13 | 5.25 ± 0.15 | 36.80 ± 0.97 | 19.3 ± 1.1 | 90.7 ± 2.9 | 0.719 ± 0.052 | 0.0203 ± 0.0016 | 2.01 ± 0.16 | 7.98 | 121 | 26.4 | | | |
| 16 | FBC/FA-2 | 10.91 ± 0.24 | 5.41 ± 0.15 | 48.2 ± 2.1 | 20.5 ± 1.2 | 85.3 ± 1.2 | 0.484 ± 0.030 | 0.0416 ± 0.0010 | 4.16 ± 0.10 | 8.40 | 95 | 26.4 | | | |
| 17 | FBC/FA-3 | 11.54 ± 0.16 | 5.31 ± 0.14 | 45.52 ± 0.31 | 18.6 ± 1.0 | 92.2 ± 2.1 | 0.332 ± 0.010 | 0.0187 ± 0.0017 | 1.87 ± 0.17 | 8.20 | 117 | 26.7 | | | |
| 18 | DB/FA-1 | 52.2 ± 1.5 | 5.37 ± 0.18 | 169.1 ± 3.4 | 8.75 ± 0.34 | 20.2 ± 1.1 | 1.39 ± 0.11 | 1.280 ± 0.059 | 128.0 ± 5.9 | 12.24 | -70 | 28.4 | | | |
| 19 | DB/FA-2 | 36.3 ± 1.3 | 8.99 ± 0.18 | 89.97 ± 0.57 | 7.46 ± 0.21 | 86.2 ± 0.62 | 2.60 ± 0.18 | 1.243 ± 0.038 | 124.0 ± 3.8 | 11.45 | -48 | 27.6 | | | |
| 20 | MSWI/FA | 31.75 ± 0.29 | 27.72 ± 0.15 | 305.8 ± 3.3 | 3.29 ± 0.24 | 97.3 ± 6.5 | 6.30 ± 0.44 | 1.40 ± 0.10 | 140 ± 10 | 12.17 | 32 | 31.7 | | | |
| 21 | CRK/FA-1 | 137.3 ± 1.7 | 48.55 ± 0.13 | 53.96 ± 0.75 | - | 94.7 ± 2.1 | 12.05 ± 0.37 | 7.79 ± 0.23 | 779 ± 23 | 10.89 | 11 | 28.4 | | | |
| 22 | CRK/FA-2 | 162.1 ± 1.8 | 55.13 ± 0.55 | 24.65 ± 0.13 | - | 242.3 ± 2.5 | 21.3 ± 1.7 | 0.129 ± 0.024 | 12.9 ± 2.4 | 10.05 | -9 | 26.1 | | | |
| 23 | CRK/FA-3 | 144.5 ± 4.4 | 48.24 ± 0.67 | 34.56 ± 0.16 | - | 228.3 ± 3.0 | 11.02 ± 0.59 | 0.0990 ± 0.0078 | 9.90 ± 0.75 | 8.46 | 90 | 26.3 | | | |

3.2. Chromium speciation

The chromium(VI) speciation analysis consisted in determination of two chromium(VI) fractions: leachable by means of a Na₂CO₃/NaOH solution and leachable by water. The first one is defined by other authors as “total content of chromium(VI)” [2], although the term “total leachable chromium(VI)” would be more appropriate. The other fraction is defined as “water soluble chromium(VI)” [26], although taking into account the fact that water extraction in fact consists in an extraction with a solution whose composition depends on chemical properties of the FA examined, we suggest an operational term “water leachable Cr(VI)”. This Cr(VI) fraction can be treated as equivalent to the availability of chromium defined by Stam et al. [3].

Keeping in mind the essence of the chromium speciation analysis procedure used, the speciation forms of chromium will be henceforth termed in a simplified manner: Cr – pseudo-total chromium, Cr(VI) – total leachable chromium(VI), Cr(III) – pseudo-total chromium(III) = Cr – Cr(VI), Cr(VI)_{sol.} – water leachable chromium(VI), and Cr(VI)_{h.leach.} – hardly leachable chromium(VI) = Cr(VI) – Cr(VI)_{sol.}

Water leachable Cr(VI) can be identified with water soluble chromates, e.g. (Na,K)₂CrO₄, (Ca,Mg)CrO₄ or ZnCrO₄, however, Cr(VI)_{h.leach.} should be identified only to a small degree with sparingly soluble chromates, e.g. BaCrO₄ or PbCrO₄. It is hard to accept the view that hot extraction with a Na₂CO₃/NaOH solution, compared to water extraction, increases the extent of CrO₄²⁻ release only due to digestion of sparingly soluble chromates. Taking into consideration the speciation of Cr(VI) in the FAs studied, the combined concentration of metals whose chromates are sparingly soluble (mainly trace elements: Ba and Pb) should be at least of the same order as the combined concentration of Na, K, Ca and Mg (major elements). Stam et al. [3] have recently paid attention to this aspect of Cr(VI) speciation as well. It is hence justified to accept the assumption that alkali extraction releases primarily Cr(VI) present in the alkali non-resistant target phase (less resistant glass or sinter) which is water-insoluble, e.g. a slagging phase according to Chen et al. [17] or a glassy phase according to Verbinen et al. [6].

The distribution of chromium species in individual FA samples is shown in Table 3. Valence speciation of Cr(III/VI) and Cr(VI) speciation are presented, with the latter in the form of water leachable and hardly leachable fractions. The results of chromium valence speciation studies for different types of furnaces were obtained by averaging all the results for FA samples collected from the same type of furnaces (Fig. 3).

In the case of the PCC boiler the chromium speciation was evaluated as an average of the results obtained for coal combustion and biomass co-combustion, because the differences appeared to be statistically insignificant. Apart from Cr(VI) determination, pH and ORP were monitored in water leachates (Table 2). The rH values oscillating around rH = 28.6 (from 26.1 to 31.7) in extracts with various Cr(VI) contents, in spite of moderate repeatability of ORP measuring, can be treated as an indication that the extraction method used makes it possible to correctly map Cr(VI) speciation in FA.

The speciation analysis has shown that the level of Cr(VI) in FA from solid fuel combustion (without CRK) was not only considerably lower than the concentration of Cr but also more spread, 2.4 ± 2.4 mg/kg (RSD = 100%), compared with 78 ± 53 mg/kg (RSD = 68%). Cr(VI) concentrations exceeding the mean value were found in FA samples from CRK, MSWI and PCC boilers, 14.8 mg/kg, 6.3 mg/kg and 5.2 mg/kg on average, respectively.

The results obtained for coal-FA are consistent with the reported Cr(VI) contents in Australian coal-FA (0.04–1.4 mg/kg) [7,8], in FA from a Dutch PCC boiler (6–9 mg/kg) [3], and in FA from a

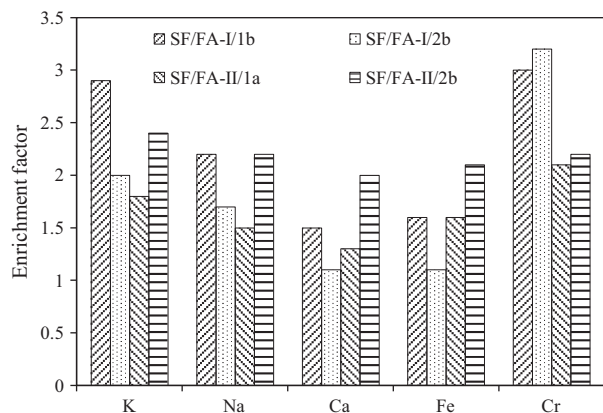


Fig. 1. Enrichment factors of the selected metals in FAs from SF boilers.

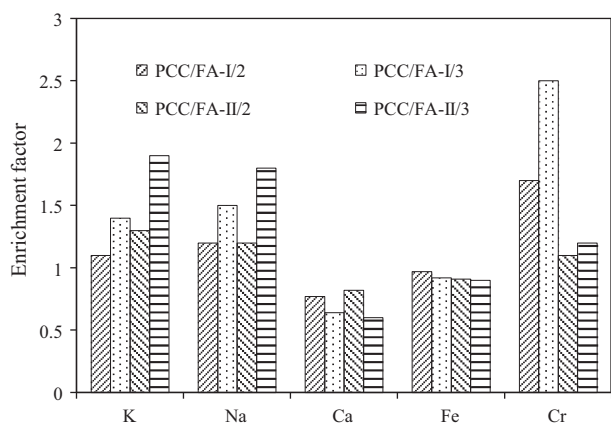


Fig. 2. Enrichment factors of the selected metals in FAs from PCC boilers.

Table 3
Chromium speciation in the fly ash samples from the different kind of the furnaces.

| No | Fly ash sample | Chromium valence speciation (%) | | Chromium(VI) speciation (%) | |
|----|----------------|---------------------------------|--------|-----------------------------|------------------------|
| | | Cr(III) | Cr(VI) | Cr(VI) _{h.leach.} | Cr(VI) _{sol.} |
| 1 | PCC/FA-I/1 | 89.5 | 10.5 | 84.2 | 15.8 |
| 2 | PCC/FA-I/2 | 88.5 | 11.5 | 69.1 | 30.9 |
| 3 | PCC/FA-I/3 | 90.4 | 9.6 | 56.2 | 43.8 |
| 4 | PCC/FA-II/1 | 90.4 | 9.6 | 49.9 | 50.1 |
| 5 | PCC/FA-II/2 | 90.9 | 9.1 | 41.6 | 58.4 |
| 6 | PCC/FA-II/3 | 92.0 | 8.0 | 36.7 | 63.3 |
| 7 | SF/FA-I/1a | 99.0 | 1.0 | 97.6 | 2.4 |
| 8 | SF/FA-I/1b | 99.5 | 0.5 | 95.7 | 4.3 |
| 9 | SF/FA-I/2a | 98.6 | 1.4 | 98.7 | 1.3 |
| 10 | SF/FA-I/2b | 99.5 | 0.5 | 96.3 | 3.7 |
| 11 | SF/FA-II/1a | 99.4 | 0.6 | 97.7 | 2.3 |
| 12 | SF/FA-II/1b | 99.7 | 0.3 | 95.2 | 4.8 |
| 13 | SF/FA-II/2a | 99.0 | 1.0 | 98.4 | 1.6 |
| 14 | SF/FA-II/2b | 99.0 | 1.0 | 97.2 | 2.8 |
| 15 | FBC/FA-1 | 99.2 | 0.8 | 97.2 | 2.8 |
| 16 | FBC/FA-2 | 99.4 | 0.6 | 91.4 | 8.6 |
| 17 | FBC/FA-3 | 99.6 | 0.4 | 94.4 | 5.6 |
| 18 | DB/FA-1 | 93.1 | 6.9 | 7.9 | 92.1 |
| 19 | DB/FA-2 | 69.9 | 30.1 | 52.2 | 47.8 |
| 20 | MSWI/FA | 93.5 | 6.5 | 77.7 | 22.3 |
| 21 | CRK/FA-1 | 87.3 | 12.7 | 35.4 | 64.6 |
| 22 | CRK/FA-2 | 91.2 | 8.8 | 99.4 | 0.6 |
| 23 | CRK/FA-3 | 95.2 | 4.8 | 99.1 | 0.9 |

Turkey Power Plant (0.2–0.3 mg/kg) [29]. The concentration of Cr(VI) in MSWI-FA (6.30 ± 0.44 mg/kg) does not differ from the

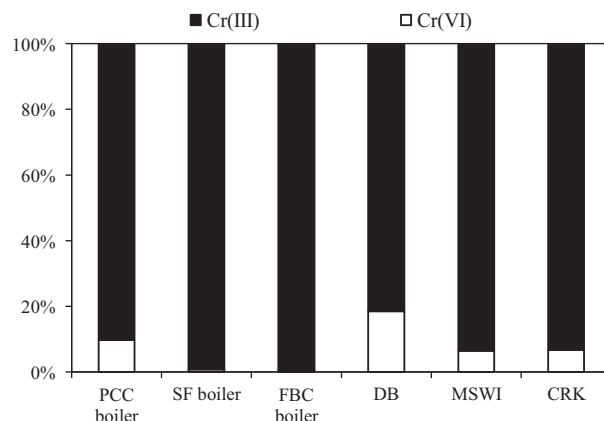


Fig. 3. Chromium valence speciation in fly ashes generated in real solid fuel furnaces based on various combustion technologies.

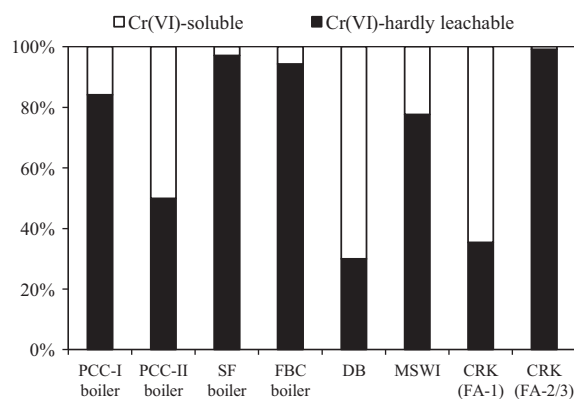


Fig. 4. Chromium(VI) speciation in fly ashes generated in the real solid fuel furnaces.

average Cr(VI) levels reported by other authors: 7.4 mg/kg [12] and ca. 8 mg/kg [30].

High percentage of Cr(VI) distinguishes wood-FA from a domestic boiler (Fig. 3). A moderate share of Cr(VI) (ca. 10%) concerns FA generated in a PCC boiler, MSWI and CRK. FA generated from coal combustion in an SF boiler and an FBC boiler are characterized by only a small (<1%) share of Cr(VI). Hence, it is justified that in mid-temperature combustion boilers the kind of fuel become a crucial factor for chromium valence speciation in the generated FA. Biomass combustion generates FA in which a significant percentage of Cr occurs as a Cr(VI) fraction. This view can also be supported by the results reported by Barbosa et al. [31] who demonstrated that co-combustion of dry sewage sludge with hard coal (1 + 1) in a BFB combustor increases the share of Cr(VI) fraction from 3% to 24% and by the results obtained by Stam et al. [3] for wood-FA from a BFB boiler, Cr(VI) – 29% and 41%.

Thus, the results of Cr(VI)_{sol.} determination turned out to be interesting (Table 2). The highest content of the Cr(VI)_{sol.} fraction can be found in FAs generated in the process of cement production, 7.79 mg/kg (FA captured in a dust chamber). Two to three times lower concentrations of Cr(VI)_{sol.} were found in the PCC-FA. It has been confirmed in studies on FA generated in two PCC boilers of the same type that co-combustion of biomass contributes to a large change in Cr(VI) speciation (Fig. 4).

The biomass/coal-FA captured in the 1st-field ESP (ca. 90% of the total amount of the collected FA) is five times more enriched in Cr(VI)_{sol.} than an analogous coal-FA fraction. The differences diminish with decreasing graining. The finest FA fractions

(3rd-field ESP, ca. 1% total mass) have a similar content of Cr(VI)_{sol.}: 3.09 ± 0.14 mg/kg (biomass/coal-FA) and 3.15 ± 0.11 mg/kg (coal-FA). About 40% lower concentrations of Cr(VI)_{sol.} were found in an incinerator-FA sample and wood-FA samples from domestic boilers. The level of the Cr(VI) fraction in coal-FA produced in SF and FBC boilers was similar and very low, from a few to a few dozen µg/kg.

The results of speciation analysis of chromium in FA samples from SF and FBC boilers justify additional remarks. A practically identical pattern of speciation of Cr (Cr(VI) – 0.8%, Cr(VI)_{sol.} – 2.9%) in FA generated in two SF boilers of the same type supplied with coal from the same source but working in different heating plants (Table 3, samples 7–14) shows good reproducibility of chromium speciation in FA generated on industrial scale. On the basis of a similar pattern of speciation of Cr in FBC-FA generated from combustion of coal from three different mines in one installation (Table 3, samples 15–17), it can be concluded that the composition of the hard coal burnt is not a critical parameter for shaping valence speciation of Cr in FA.

3.3. Formation of chromium(VI) during fuel combustion

Based on the speciation analysis of chromium it can be concluded that the technological factors which are conducive to a higher Cr(VI) content in FA are combustion of biomass and a high combustion temperature. The key to explaining these observations is a mechanism of chromium transformations taking place in the process of fuel combustion. The base for a description of the mechanism was to assume that transport of chromium, irrespective of combustion technology, proceeds according to a mixed mechanism in which a major role was played by a volatilization–condensation/adsorption stage. In our work the correctness of this assumption was confirmed by increasing concentrations of chromium in finer fractions of FA generated both in the process of high-temperature coal combustion (PCC/FA samples) and in the stoker-fired boilers (SF/FA samples). Finer particles have larger surface areas, which allows more effective deposition of volatile species on their surface. Our observations are not isolated, although they are not always interpreted identically [8,23]. Following Stam et al. [3] and Chen et al. [17] we assume that organic forms of Cr(III) present in fuels were responsible for volatility of chromium. In a combustion chamber, depending on local oxidizing and temperature conditions, gaseous Cr(III)-org. undergoes pyrolysis to Cr(III)-inorg. and, partially, oxidation to Cr(VI). Cr(III/VI) species which are thermodynamically stable under combustion conditions include CrOOH_(g), and CrO_{3(g)} and CrO_{2(OH)_{2(g)}}, respectively [3,18,32]. It has been confirmed experimentally that CrO_{2(OH)_{2(g)}} was a dominant volatile species when Cr₂O₃ is exposed to H₂O and O₂ at high temperatures [33]. Thereby, one can expect that CrOOH and CrO_{2(OH)₂} will be the main gaseous species in the combustion zone.

As Cr(VI) concentration in the FA studied also increases with diminishing graining (see also [8,29]), one can justify that Cr(III) undergoes oxidation in the gaseous phase, although it should be kept in mind that oxidation of CrOOH deposited on the surfaces of FA particles, e.g. $2\text{CrOOH} + 2\text{Na}_2\text{O} + 3/2\text{O}_2 \rightarrow 2\text{Na}_2\text{CrO}_4 + \text{H}_2\text{O}$ was also superficial in nature [17].

It should be noted that there is a divergent tendency for enrichment factors of Cr(III) and Cr(VI) determined for grain fractions of PCC-FA and SF-FA generated during coal combustion (Fig. 5). Similar values of EF-Cr(III) and EF-Cr(VI) directly suggest the oxidation of Cr(III) in the gaseous phase and deposition of the generated Cr(VI) species on FA particles, whereas EF-Cr(VI) < EF-Cr(III) can be interpreted as a result of reduction of Cr(VI) at the surface reaction stage. Hence, the reasons for a low content of Cr(VI) in SF-FA can be related to the chemical composition of the surface layer of FA particles. As demonstrated above, the operating conditions in

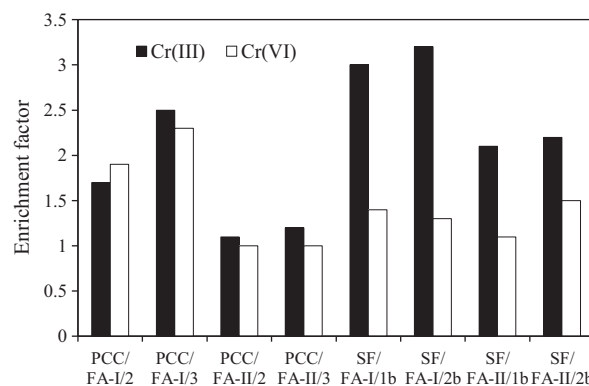


Fig. 5. Enrichment factors of Cr(III) and Cr(VI) in FAs from PCC and SF boilers.

SF boilers are conducive to the formation of a coating enriched with Ca, Cr, K, Na and Fe, whereas the surface of PCC-FA particles should be enriched only with Na, K and Cr.

Based on thermodynamic considerations by Fernández et al. [25], it can be assumed that under high-temperature combustion conditions Fe was not volatilized in the combustion chamber, but was mainly present inside the glass matrix or the coating glass matrix of the FA, and its deposition on the surface of FA particles was minimal. These assumptions are consistent with the results of the study by Kutchko and Kim [28] who demonstrated that PCC-FA comprised mainly of amorphous aluminosilicate spheres and a smaller amount of iron-rich spheres, and the majority of the latter exist as mixed iron oxide/aluminosilicate particles.

Transport of Fe should proceed differently in the flue gas of an SF boiler. In this case, it can be expected that the formation–volatilization–condensation of Fe(II) chloride plays an important role (Fe(III) chloride is not stable above 315 °C). Although above 800 °C (typical of an SF boiler combustion chamber) iron can exist as chloride and oxide [25], the surface of FA particles would be enriched primarily with iron oxides due to surface reactions e.g.: $\text{MCl}_2 + \text{H}_2\text{O} = \text{MO} + 2\text{HCl}$ [34].

Fe oxides accumulated on the surface of SF-FA particles may lead to a low content of Cr(VI) in FA not only by reducing the Cr(VI) species but also by binding the Cr(III) species. The correctness of this reasoning can be confirmed by the results of Jiao et al. [18] who have shown that the percentage of FeCr₂O₄ in fine FA particles generated from coal combustion at 1000 °C was considerably higher than in coarse particles. Stam et al. [3] have reported that the spinel phase (Fe,Mg)(Fe,Al,Cr)₂O₄ was a dominant form of Cr in FA generated by mid-temperature combustion. Recently, Chen et al. [5] have revealed that Fe₂O₃ effectively inhibits oxidation of Cr(III) by forming the corresponding chromites.

The high level of Cr(VI) in PCC-FAs is a clear indication that high combustion temperature (>1500 °C) during pulverized coal combustion is the factor which significantly shapes chromium valence speciation. The thermal conditions ensuring intensive vaporization of alkali metal compounds (e.g. KOH bp. 1320 °C, NaOH bp. 1390 °C, NaCl bp. 1413 °C and KCl 1500 °C subl.) are thus conducive to both stabilization of Cr(VI) and oxidation of Cr(III) captured in the alkaline aerosol being formed.

The stabilization of Cr(VI) in melted alkalis was probably important in all solid fuel combustion processes. Opila et al. [33] have shown experimentally that in the absence of stabilizing substances, CrO_{2(OH)₂} condenses at the temperature of ≤600 °C as hexavalent Cr and at ≥700 °C as Cr₂O₃. So, one can expect that the Cr(VI) content in FA was a consequence of the stabilizing action of alkali metals and a complex action of iron oxides which, under favorable conditions, can effectively prevent oxidation of Cr(III).

Based on our reasoning presented above, one can expect that the surface composition of PCC-FA should be conducive to oxidation of Cr(III) to Cr(VI) rather than the surface composition of SF-FA. A supplementary experiment was performed in order to positively verify this statement. Two samples of FA ($m = 0.5$ g): the PCC/FA-II/1 and SF/FA-II/1a with similar Cr contents (51.8 mg/kg and 48.7 mg/kg, respectively) were heated in a muffle furnace at 700 °C for 2 h. The concentration of Cr(VI) increased in both samples and there was 10 times more Cr(VI) in the PCC/FA-II/1 sample than in the SF/FA-II/1a sample (3.3 mg/kg vs. 0.32 mg/kg). The result corresponds well not only with the Cr speciation in the FA studied, but also with the recent results obtained by Chen et al. [5].

In order to simplify the picture of chromium transformation during solid fuel combustion in real furnaces the attention was put on the factors which are critical for the formation of Cr(VI). The well-known effect of CaO on the formation of Cr(VI) during thermal treatment of wastes was omitted due to a high melting point (m.p. 2572 °C) eliminating the participation of vapor CaO in alkaline aerosol and due to a lower, compared to KOH and NaOH, ability to form chromates under combustion chamber conditions [6].

4. Conclusion

The study of the presence of Cr(III), Cr(VI), water leachable Cr(VI) and hardly leachable Cr(VI) in FAs from 6 types of furnaces used in power industry, heat engineering, municipal waste treatment and cement production allowed for an assessment of the effect of solid fuel combustion technologies on chromium speciation in the generated FAs. It was shown that the technological factors which are conducive to a higher Cr(VI) content in FA were the combustion of biomass and a high combustion temperature. Confronting the results of the Cr speciation analysis obtain with this work with those reported by other it has been shown that hard coal combustion in SF, FBC or domestic boilers should generate FA with a low level of Cr(VI), because, under these conditions, Fe oxides effectively prevent oxidation of Cr(III). Replacing fuel with biomass should promote chromium evaporation while a high content of alkali metals and a low level of Fe, characteristic of biomass, would create favorable conditions for stabilization of Cr(VI) being formed and for oxidation of Cr(III) deposited on the surface of FA particles. As a result, FA has a higher content of Cr(VI). High Cr(VI) concentrations can be expected also in FA generated by high-temperature coal combustion in PCC boilers. Under these conditions oxidation of Cr(III) was favored due to deactivation of Fe oxides and an increase in evaporation intensity of alkali compounds. Municipal solid waste incineration should generate FA in which Cr speciation will be very similar to the one obtained in FA generated during combustion of biomass in heating boilers, although, in this case, the kind and composition of the municipal waste fraction introduce considerable uncertainty to predictions.

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